Characterization of a Spin-Applied Dielectric for Use in Multilevel Metallization

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ABSTRACT

The spin-applied polysiloxane film Futurrex IC1-200 has been examined for use as a planarizing component of the dielectric layers of high density integrated circuits utilizing multiple levels of interconnecting metallization. The thickness of the as-spun film varies significantly with cure: it is invariant after thermal curing at 190°C in vacuo or 250°C in air and after additional curing at 450°C in N₂ or Ar. However, the index of refraction decreases from 1.414 after curing at 190 C to 1.340 after curing at 450°C in either inert ambient. Treatment of the thermally cured films (190° or 450°C) with an O₂ plasma for 30 min in a barrel reactor results in a decrease in thickness of ~40% and a concomitant increase in the index of refraction from 1.414 to 1.438. Despite this large reduction in thickness, the stress of the film is low (1.7 × 10⁹ dyn/cm², tensile) after O₂-plasma curing. Etch rates of the thermally and O₂-plasma cured films in HF and P-etch solutions suggest that the organosilicon material becomes porous and inorganic-like after exposure to the O₂ plasma in a barrel reactor. This is supported by the Fourier transform infrared (FTIR) spectra of the material; after curing in an O₂ plasma the band assigned to CH₃ substituents of the polysiloxane is absent, while a band at 1060 cm⁻¹, which is close to the position of the Si—O—Si stretching vibration in SiO₂, sharpens and increases in intensity. In addition, although the FTIR spectra of the films cured at 190°C in vacuo or at 450 C in N₂ are featureless from 3100 to 3600 cm⁻¹, that of the O₂-cured film exhibits a small, broad absorption in this region, suggestive of the presence of absorbed water or the formation by hydrolysis of Si—OH moieties in this apparently more porous framework.

As devices are reduced to smaller dimensions and the complexity of integrated circuits increases, the area which is allocated to the device interconnection network becomes a significant impediment to continued dimensional scaling (1). This limitation may be alleviated and greater circuit flexibility may be realized by the use of multiple levels of interconnecting metallization (2-4). However, for high density circuits with tight metal pitches and narrow metal lines (~ <2 μm), the topography is so severe that dimensional control of lines formed over steps may be compromised. This results in (i) narrowing ("necking") of metal lines, (ii) physical discontinuities along metal lines which traverse very abrupt steps, and (iii) generally poorer feature resolution, all of which may lead to higher circuit resistance as well as inter- and intralevel metal shorting.

These limitations on circuit performance and circuit design which are imposed by extreme topography may be overcome by smoothing or planarizing the dielectric layers which separate levels of metallization by the etchback approach (5). However, planarization of a dielectric of a high density circuit which is formed by conventional low pressure chemical vapor deposition (LPCVD) by this commonly employed method is particularly challenging because this deposition technique essentially replicates the underlying uneven topography. In addition, since the temperature for deposition of the dielectric over aluminum metallizations cannot exceed ~600°C, the resulting step coverage is semiconformal, leading to cusps and stress within the dielectric at the base of abrupt steps and to the formation of voids within the film between closely spaced features of significant step height (~ ≥ 5000Å) (6).

All of these dielectric planarization constraints (virtual application of nonplanar substrates, nonconformal step coverage, and void formation) may be alleviated by the use of a spin-applied dielectric (7-9) in conjunction with a conventional low temperature LPCVD film, such as SiO₂, to form a hybrid intermetal dielectric film. In this paper, we describe the characterization of a commercially available spin-coated polysiloxane [R₃Si—O—(—SiR₂—O—)ₙ—SiR₃, R = CH₃, C₆H₅...], Futurrex IC1-200,² which has been used in a planarization process developed for the extremely severe topography of high density CMOS circuits which use interconnecting metal pillars and 1 μm wide metal lines and spaces for all levels of metallization (10, 11).

Experimental

Films of Futurrex IC1-200 were formed on 4 in. diam silicon wafers of [100] orientation by spin coating at 3000 or 6000 rpm. The films were then cured by baking on a hot plate at 190°C in vacuo for 45s. Additional curing was performed for some samples in a convection oven at 250°C for 30 min, in a quartz furnace in a N₂ ambient at 450°C for 30 min, by rapid thermal annealing at 450°C for 2-4 min, or in a barrel reactor in an O₂ plasma (12, 13) for 2-30 min. Film thickness and refractive index as a function of cure were determined simultaneously with a Gaertner Scientific Company L116 ellipsometer (HeNe laser, 6328Å) or with a Rudolph Research EI IV ellipsometer (5461 and 6328Å). Film thickness uniformity after thermal and plasma curing was assessed with an IBM 7840 Film Thickness Analyzer using the refractive index determined by ellipsometry and a 14 point concentric grid with the orientation of the wafer fixed by the apparatus, or with a five point pattern with the Rudolph ellipsometer in which the refractive index and the film thickness were determined at each point using the two wavelengths given above. The appropriate thickness was then obtained by a thickness matching algorithm of the software which supports the ellipsometer (14).

Etch rates of Futurrex IC1-200 as a function of cure were determined in 6:1 NH₄F-buffered HF solution and P-etch solution (15) at room temperature (20° ± 1°C).

Stress measurements, also as a function of cure, were made with ultraflat (<0.5 μm nonlinear thickness variation over a 50 mm scan) 4 in. diam silicon wafers of [100] orientation by the radius of curvature method (16-18) in which the stress, σ, is given by Eq. [1]

$$\sigma = \{[E_s/6(1 - v_s)](t_1^2/t_f)(1/R)\}$$ [1]

where E_s (1.055 × 10¹² dyn/cm²) and v_s (0.446) are Young's modulus and Poisson's ratio for the silicon substrate, t_1 and t_f are the thicknesses of the silicon wafer and the spin-dielectric film, respectively, and R is the radius of curvature of the wafer. The value of R for the uncoated wafer was determined from a 50 mm trace with a Sloan Dektak II profilometer centered at the middle of the wafer. The value of R resulting from stress of the film was then determined by subtracting the amplitude of the profilometer trace at the center of the wafer after spin application of the film onto the wafer from that measured along the same 50 mm trace before application of the film.

Infrared spectra of the films as a function of cure were gathered in the absorbance mode using a Nicolet Analytical Instruments 60SX Fourier transform spectropho-

Table I. Thickness and index of refraction (at 6328Å) of Futurrex IC1-200 as a function of cure as determined by ellipsometry

Process*	Thickness (Å)	Index of refraction
Hot plate bake at 190°C, 45s	1422 ± 9	1.414 ± 3
Hot plate bake at 190°C, 45s; 450°C in N₂, 30 min	1432 ± 4	1.337 ± 5
Hot plate bake at 190 C, 45s; 450°C in N₂, 30 min; O₂ plasma, 30 min	864 ± 2	1.429 ± 2
Hot plate bake at 190 C, 45s, O₂ plasma, 30 min	886 ± 8	1.438 ± 2

* Films were spin-coated at 6000 rpm. O₂ plasma conditions: Tegal Plasmaline 415 system operated at 1 torr of O₂ and 300W of RF power at 13.56 MHz.

tometer (FTIR). To minimize scattering of the infrared radiation from an irregular substrate, the films were applied to silicon wafers which were polished on both sides.

Discussion

Film thickness and index of refraction as a function of type of cure are given in Table I. Upon prolonged exposure to an O₂ plasma, the Futurrex IC1-200 film shrinks by ~40% from its initial thickness. As shown in Fig. 1 and 2, most of this shrinkage occurs within the first 2-5 min of exposure. The index of refraction (at 5461Å) changes in a manner which is similar but opposite to that of film thickness (see Fig. 1). Its value after cure at 190°C on a hot plate in vacuo of 1.414 ± 3 increases sharply to 1.428 ± 2 after exposure to an O₂ plasma in a barrel reactor for ~3 min. It then rises slowly to 1.438 ± 2 after a total of 30 min of O₂ plasma treatment (19). Curing at 450°C, either in dry N₂ in a furnace or in Ar by rapid thermal annealing after the initial baking at 190°C, reduces the refractive index to 1.337 ± 5 and 1.340 ± 4, respectively. As shown in Table I, the film thicknesses after curing at 190°C and then after additional curing in N₂ are not significantly different. The decrease in refractive index after the higher temperature treatment, although suggestive of an increase in the porosity of the film, may be the result of loss of either moisture or residual solvent or some degree of cross-linking of the polysiloxane at this higher temperature. Subsequent cure in an O₂ plasma of either the N₂- or the Ar-cured film yields the same increase in refractive index and concomitant film shrinkage as observed upon direct O₂ plasma exposure without an intermediate treatment in an inert ambient (see Table I).
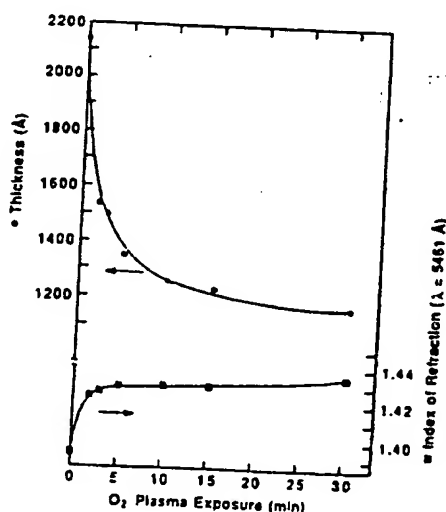

Fig. 2. Film thickness ● (left-hand side) and etch rate ■ (right-hand side) of Futurrex IC1-200 in 6:1 NH₄F-buffered HF solution as a function of exposure to an O₂ plasma in a barrel reactor. Plasma conditions and spin speed are given in the caption of Table I. Wafers were baked on a hot plate at 190°C for 45s before plasma treatment.

As shown in Fig. 2, after only 2 min in the O₂ plasma, the HF etch rate approaches that of undoped LPCVD SiO₂ (~2000 Å/min). This is similar to the behavior of other spin-applied organosilicon materials which have been cured in an O₂ plasma in a barrel reactor (12). However, after 10 min of O₂ plasma exposure, the etch rate of the film in HF solution increases markedly. Moreover, as shown in Table II, the etch rate of the material in P-etch solution (15) increases at an even greater rate than that in HF solution after exposure to the O₂ plasma. Such etch rate behavior with various deposited SiO₂ films has been ascribed to porosity or Si—O bond strain in SiO₂ networks (20-22). For this spin-applied film, however, the high etch rates are probably a consequence of both appreciable film porosity and chemical conversion of the as-spun organosilicon material to a more inorganic-like film by the O₂ plasma. In contrast, films of Futurrex IC1-200 which have been cured at 450°C in N₂ or Ar, while exhibiting the decrease in refractive index noted above, etch very slowly in P-etch solution, at rates which are equal to that of thermally grown SiO₂ (15, 20, 21). Hence, the films of Futurrex IC1-200 which are not exposed to the reactive oxygen atoms of an O₂ plasma in a barrel reactor appear to be contiguous, low in porosity (despite the apparent decrease in refractive index), and presumably highly amorphous. Under the conditions of the O₂ plasma, the reaction between the film and the oxygen atoms which diffuse through the film (13) may

Fig. 1. Film thickness ● (left-hand side) and index of refraction ■ (at 5461Å) (right-hand side) of Futurrex IC1-200 as a function of exposure to an O₂ plasma in a barrel reactor. Plasma conditions are given in the caption of Table I. The material was applied to the wafers in the static mode and then formed by spinning at 3000 rpm.
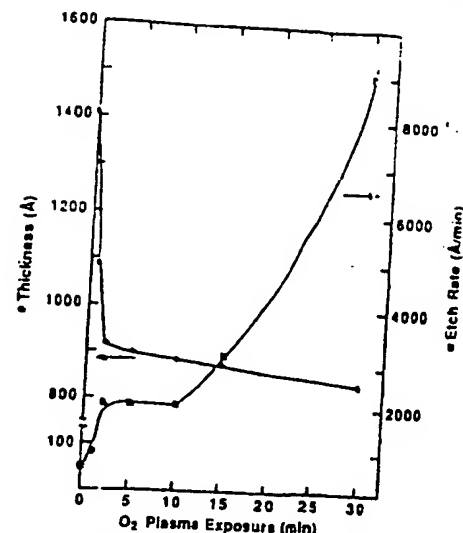
Table II. Etch rate of Futurrex IC1-200 in P-etch solution as a function of cure*

Curing procedure[b]	P-etch rate (Å/s)[c]
190°C (45s)	
190 C (45s), N₂ at 450°C (30 min)	~3
190°C (45s), Ar at 450°C (4 min)[d]	~2
190°C (45s) O₂ plasma (2 min)	~3
O₂ plasma (5 min)	~100
O₂ plasma (10-30 min)	~115
N₂ at 450°C (30 min), O₂ plasma (30 min)	>250
	>250
Thermal SiO₂[e]	2

* Composition of P-etch solution is given in Ref. (15).
[b] Curing at 190°C was performed on a hotplate; curing in N₂ was performed in a quartz furnace as described in text.
[c] Temperature of the solution was 21 ± 1°C.
[d] Curing in Ar was performed by rapid thermal anneal techniques with an AG Associates Heatpulse 210.
[e] See Ref. (15)

Table III. Stress of Futurrex IC1-200 with cure

Initial film thickness (Å)[a]	Cure	Stress (dynes/cm²)
5602	190°C	0.24 · 10⁹ (tensile)
5172	190°, 450°C	0.68 · 10⁹ (tensile)
4520	190°, 450°C, O₂, 1 min	0.95 · 10⁹ (tensile)
4003	190°, 450°C, O₂, 5 min	1.7 · 10⁹ (tensile)
1125[b]	190°C, O₂, 30 min	1.3 × 10⁹ (tensile)
2820	CVD SiO₂[c]	1.3 × 10⁹ (compressive)
2820/1316[d]	190°, 450°C, O₂, 30 min	0.6 × 10⁹ (compressive)

[a] Three successive coatings at 3000 rpm unless indicated otherwise.
[b] One coating applied at 3000 rpm.
[c] Undoped SiO₂ deposited by LPCVD methods at 380°C by reaction of SiH₄ and O₂.
[d] Composite structure composed of 2820Å undoped LPCVD SiO₂ covered with 1316Å of Futurrex IC1-200 which was baked at 190°C for 45s, and then cured at 450°C in N₂ and in an O₂ plasma.

produce a porous structure which is more easily attacked by HF and P-etch solutions than the film which is cured in an inert environment of N₂ or Ar. In addition, the films which were cured in an O₂ plasma were also shown to etch at a very high rate in a CF₄-based plasma in a parallel plate reactor, as might be expected for a porous material composed of silicon, oxygen, and carbon. In comparison, when cured at 190°C in vacuo, Futurrex IC1-200 etches at ~4300 Å/min in the CF₄ plasma of the parallel plate reactor (23), which is significantly less than the etch rate of the film after exposure to the O₂ plasma of the barrel reactor (>10,000 Å/min).

As noted above (see Table I and Fig. 1 and 2), the Futurrex IC1-200 film shrinks dramatically upon exposure to an O₂ plasma. Despite this large reduction in thickness, the stress in the film remains low (see Table III), increasing slightly with both thermal and plasma cure but reaching a value which is similar in magnitude but opposite in sign to that of undoped LPCVD SiO₂, formed at 380°C by the reaction of SiH₄ and O₂. Consistent with this is the observation that the films treated with an O₂ plasma crack on unpatterned wafers only at as-spun thicknesses greater than ~0.35 μm. Films which were applied at thicknesses <0.2 μm directly over 0.7 μm high steps consisting of 1.0 μm lines and spaces did not exhibit cracking. Since films with thicknesses between 0.2 and 0.35 μm were not examined, their stress relief behavior (i.e., cracking) is not certain. However, significantly thicker films (>0.35 μm) obtained by multiple spin-coatings at 3000 rpm per coat showed pronounced cracking over this topography.[3]

The FTIR spectra of the cured films are presented in Fig. 3 and 4. As shown in Fig. 3, the spectra after curing at 190°, 250°, and 450°C are virtually superimposable from 280 to 1810 cm⁻¹, indicative of no detectable change in the content or composition of the film over this temperature range. After exposure to an O₂ plasma, the absorptions at 1272 cm⁻¹ are absent, while absorptions near 1025 and 1110 cm⁻¹ of the thermally cured film coalesce at ~1060 cm⁻¹ (see Fig. 4). The peak at 1272 cm⁻¹ has been assigned to C—H vibrations of CH₃ substituents (12) of organosilicon films, while that at ~1060 cm⁻¹ is close to the Si—O—Si stretching vibration (21, 24) in undensified LPCVD SiO₂ (top spectrum in Fig. 3). As discussed by others (21 24), the position of the Si—O—Si stretching vibration in deposited SiO₂ varies with stoichiometry, ranging from ~940 cm⁻¹ in oxygen deficient films to ~1075 cm⁻¹ in stoichiometric SiO₂. It is noteworthy that, as shown in Fig. 4, the FTIR spectra of the films which were not exposed to the O₂ plasma are featureless from ~3100 to 3600 cm⁻¹, while that of the film exposed to the plasma displays a broad, low intensity band in this region. These latter absorptions may be due to the presence of water and Si—OH groups (21)

Thicker films were obtained by successively spinning at 3000 rpm and baking at 190°C for 45s on a hot plate with no other form of curing between spin applications.

FTIR Spectra of Futurrex IC1-200

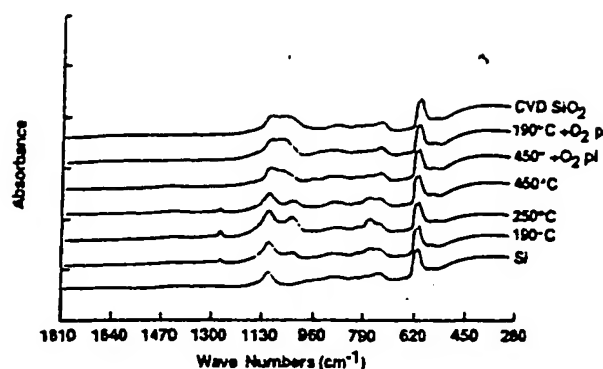
Fig. 3. FTIR spectra of thin films of Futurrex IC1-200 between 280 and 1810 cm⁻¹ on double-polished single-crystal silicon wafers as a function of cure. Film thicknesses, as a function of cure, are given in Table I. The bottom spectrum is that of the double-polished single-crystal silicon wafer; the top spectrum is that of undoped LPCVD SiO₂, deposited at 380°C by reaction of SiH₄ and O₂.
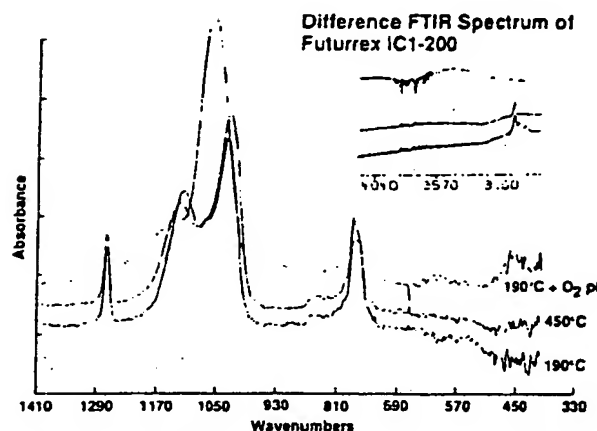

Fig. 4. Difference FTIR spectra of thin films of Futurrex IC1-200 between 330 and 1410 cm⁻¹ on double-polished single-crystal silicon wafers as a function of cure. Film thicknesses, as a function of cure, are given in Table I. The absorptions of the silicon substrate have been subtracted from these spectra. The lower spectrum is after thermal cure at 190°C on a hot plate for 45s; the middle spectrum is after an additional thermal cure at 450°C in N₂ for 30 min; the upper spectrum is after thermal cure at 190°C on a hot plate for 45s and plasma cure in O₂ in a barrel reactor for 30 min. The spectra of these films, in the same order, from 2700 to 4100 cm⁻¹ are shown in the upper right-hand corner. The broad absorption of the O₂ plasma-cured film (top spectrum) may be due to bound water as well as the Si—OH groups formed from absorbed moisture.

which may have formed as a consequence of the absorption (and subsequent reaction) of atmospheric moisture by a porous film.

Conclusion

The behavior of Futurrex IC1-200 as a function of thermal and O₂ plasma curing is somewhat puzzling. The increase in the index of refraction and the concomitant decrease in the film thickness with O₂ plasma exposure suggests that the material has been densified by this treatment, a conclusion which would appear to be consistent with the coalescence, sharpening, and increase in intensity of the FTIR absorptions at ~1060 cm⁻¹. On the other hand, the extremely high etch rates of the films after O₂ plasma treatment is suggestive of a porous, low quality unden-

sified film." Indeed, the presence of a very broad, low intensity absorption band at 3100-3600 cm^{-1} only for the O$_2$-cured film is evidence for the existence of absorbed water molecules and bound OH groups (as Si—OH) within a porous medium. The changes in the FTIR spectra between ~1000 and ~1300 cm^{-1} after O$_2$ plasma treatment imply that additional oxygen atoms have been incorporated into the film and that the concentration of methyl substituents of the polysiloxane has been diminished by oxidation; that is, the film is now more inorganic. The position and narrowness of the band at ~1060 cm^{-1} is probably a consequence of higher oxygen content and hence more Si—O—Si bonding in a less strained, porous network. Although the FTIR spectra of the films after thermal treatment (190°, 250°, and 450°C) are virtually identical, the change in index of refraction (see Table I) with temperature suggests that a reaction, possibly incipient polymer cross-linking, occurs between 190° and 450°C.

Interestingly, the increase in tensile stress of the film with O$_2$ plasma exposure might not be expected for an undensified, porous film. Presumably, this increase in stress, despite apparently greater porosity, may be due to a greater disparity in the linear coefficients of thermal expansion (21) of the silicon substrate and the O$_2$-cured film than exists for those films of Futurrex IC1-200 which have not been exposed to this plasma.

As described elsewhere (10), incorporation of this material at a thickness of ~0.2 μm (single coating at 3000 rpm) as a component of the intermetal dielectric has yielded significantly improved topography after resist etchback planarization. In addition, application of the film over severe topography prior to low temperature LPCVD of SiO$_2$ results in the elimination of voids between closely spaced underlying features and the necessary electrical isolation between adjacent metal layers. Moreover, the dielectric surfaces produced prior to resist etchback planarization are substantially more amenable to planarization since the severe topography has been smoothed with a spin-applied film (10) before the etching process is begun. Finally, as shown in Table III, the formation of composite structures (25) consisting of a deposited SiO$_2$ layer above or below a coating of Futurrex IC1-200 may yield dielectric layers which are particularly low in stress, since the deposited film and this spin-applied film are similarly but oppositely stressed. This effect is advantageous for very high density multilevel metal integrated circuits (18).

Acknowledgments

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